SYNTHESIS OF PRUSSIC ACID

Part 17

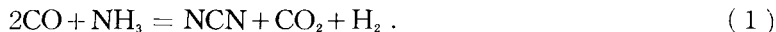### Deactivation and Regeneration of Alumina-Thoria Catalyst

By

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Introduction

It is already known that various metal oxides such as alumina, thoria, urania, and magnesia are catalytically active toward synthetic reaction of hydrogen cyanide from carbon monoxide and ammonia, $i.e.$,

$$2CO + NH_3 = NCN + CO_2 + H_2 . \qquad (1)$$

HORIUTI, $et\ al.$[1] have provided an improved process for raising the yield of hydrogen cyanide which is carried out under pressure, high space velocity, and relatively low temperature in the presence of alumina-thoria containing a small amount of sulfate as catalyst. It was found by KINOSHITA, $et\ al.$[2] that the same catalyst maintains a constant cyanide yield for at least 300 hours at 650°C, but that the yield at 650°C decreases to half once the catalyst is used for 15 hours at 850°C.

In this work such deactivated catalyst has been found to be easily regenerated by sulfuric acid or water treatment to a considerable extent. Crystal structures, surface areas, sulfur contents, $etc.$ were measured with the catalyst to investigate the deactivation or regeneration process.

§ 1. Materials and Apparatus

A flow diagram for hydrogen cyanide synthesis is shown in Fig. 1.

Carbon monoxide was generated and purified as follows. Concentrated sulfuric acid was dropped into formic acid chilled by wet ice. The mixture was then warmed up to 40°C to generate carbon monoxide. The gas was passed through 50% potassium hydroxide, over glass wool, and then stored in a large reservoir. It was forced out from the reservoir by water and passed over a purification train consisting of : (a) zinc oxide-chromia mixed catalyst heated at 400°C for the conversion of impurity oxygen into carbon dioxide ; (b) soda

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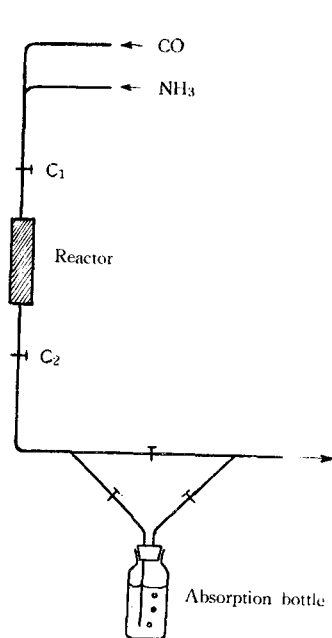[*] Research Institute for Catalysis, Hokkaido University.

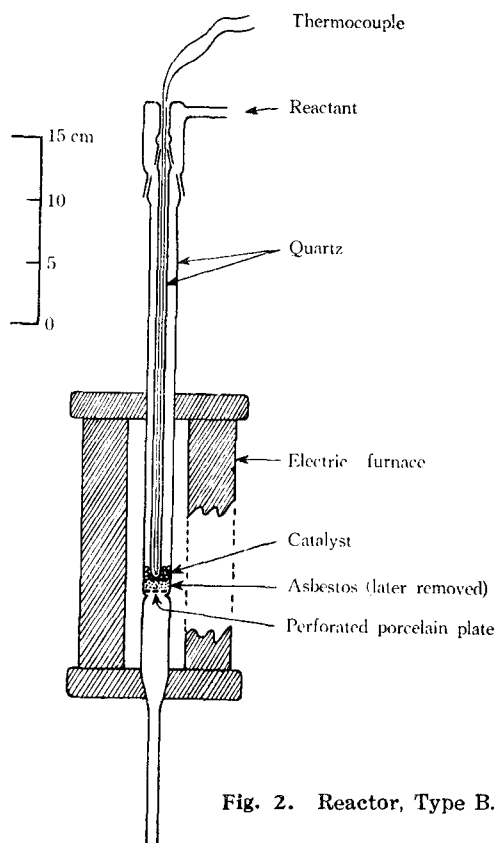Fig. 1. A schematic flow diagram for hydrogen cyanide synthesis.

Fig. 2. Reactor, Type B.

lime; (c) liquid oxygen trap. Both (b) and (c) served to remove water and carbon dioxide.

The condensation of cylinder ammonia was evaporated from a trap with a bubble type pressure regulator by means of alcohol bath kept at *ca.* $-30°C$. Gaseous ammonia thus obtained was passed over soda lime for drying.

Catalysts I and II were separately prepared by the same method as described in the reference (1a) so as to contain 3 weight percent thoria on alumina-thoria basis[*]. Calcination was carried out for 3 hours at 750°C. Portions of 8 to 14 mesh were used.

A mixture of carbon monoxide and ammonia was passed over a flow type reactor, type A or type B. Type A is identical with the reactor used in the

[*] Three percent ammoniacal water was added to a mixed solution of ammonium alum and thorium nitrate until the pH of the solution reached 9 in the case of catalyst II, but the final pH was not measured in the case of catalyst I.

previous work[3]. Type B with 18 mm inner diameter is illustrated in Fig. 2.

Gas leaving the reactor was led either directly into a hood or into an absorption bottle containing 100 cc of 1 N potassium hydroxide or 0.3 N sulfuric acid.

§ 2. Experimental Procedures

HCN Synthesis

The synthesis was conducted in the flow system shown in Fig. 1 at a temperature range of 650 to 950°C at ordinary pressure. Cyanide yield was always determined only at 650°C throughout the present experiments. High temperatures at or over 800°C were employed for the deactivation of the catalyst. Feed rates of reactants were fixed at 100cc/min of carbon monoxide and 10 cc/min of ammonia, both in S.T.P. At the beginning of the synthesis, the catalyst temperature was gradually raised in the feed stream up to a required temperature. At the conclusion of the synthesis the feed stream was maintained until the catalyst temperature lowered down to 150°C, then the stopcocks C_1 and C_2 of Fig. 1 were turned to shut off the catalyst from the air. Time was allowed until the catalyst temperature fell to room temperature in case of taking the catalyst out of the reactor.

Analyses of Gas

Analyses were made for hydrogen cyanide and unreacted ammonia as well as for hydrogen sulfide, which was often liberated from the catalyst during the synthesis. The gas leaving the reactor was bubbled for one hour through 1 N potassium hydroxide when analyzing it for hydrogen cyanide or hydrogen sulfide, and through 0.3 N sulfuric acid when analyzing it for ammonia. An aliquot of the solution was analyzed as follows.

H_2S.—Hydrogen sulfide was detected by adding lead acetate to an aliquot.

HCN.—When sulfide was absent, another aliquot was diluted 10 times with water and then immediately titrated with 0.1 N silver nitrate according to LIEBIG-DENIGÈS[4]. When sulfide was present, one or two drops of 10% lead acetate were added to another diluted aliquot, time was allowed for the disappearance of the brown tinge of lead sulfide, and then the titration was carried out. It was shown separately that this procedure gives an accurate cyanide determination even in the presence of 10^{-4}N sulfide.

Unreacted NH_3.—Microdiffusion analysis was carried out according to CONWAY[5] with an aliquot.

Treatment of Catalyst

Pretreatment.—According to KINOSHITA, *et al.*[2] it takes about 8 hours

at 650°C with freshly prepared catalyst until the evolution of hydrogen sulfide decreases to some minor extent and simultaneously the cyanide yield increases up to a steady value. In the present work, therefore, fresh or sulfuric acid-treated catalyst was pretreated for two to ten hours at 650°C in a reactant stream prior to the cyanide determination.

Heat Treatment.—The deactivation of catalyst by the cyanide synthesis at or over 800°C will be called "heat treatment" in what follows.

H₂SO₄ treatment.—Catalyst was boiled for five minutes with 100 cc of 1 N sulfuric acid. After cooling the supernatant liquid was decanted and the catalyst was dried for one hour at 100°C.

H₂O Treatment (a).—This was carried out just in the same manner as sulfuric acid treatment, using redistilled water instead of 1 N sulfuric acid.

H₂O Treatment (b).—Catalyst was refluxed for 30 minutes with 500 cc of redistilled water. While hot the supernatant liquid was decanted and the catalyst was dried for one hour at 100°C.

Determination of Sulfur Content and Surface Area of Catalyst

Total Sulfur.—Total sulfur content was determined by KIBA's method[6]. The method consists of the following three successive steps: (a) reduction of sulfur of any forms to hydrogen sulfide by a new reducing agent, tin (II)-strong phosphoric acid, (b) absorption of the hydrogen sulfide by zinc acetate solution, (c) determination of the resulting zinc sulfide either by the ordinary iodometric titration or colorimetrically by the methylene blue method.

Sulfide Sulfur.—For the determination KIBA's method was modified only in the step (a) as follows; sulfide sulfur present in a sample was released as hydrogen sulfide by strong phosphoric acid with no reducing agent[*].

Surface Area.—The determination was made by a conventional BET method using nitrogen adsorbate at the liquid nitrogen temperature after a sample was evacuated for one hour at 400°C.

Series

Three series of experiments were carried out renewing the catalyst every time. In each series the catalyst was subjected to alternate treatments of heat and sulfuric acid or water, and the cyanide yield was measured after each treatment. In series 1 measurements were taken also of the crystal structure of the catalyst and the loss in weight of the catalyst during the treatments. In series 2 and 3 the surface area and the sulfur content of the catalyst, and the quantity of unreacted ammonia were measured. They are detailed as follows.

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*) Neither barium chloride solution nor barium hydroxide solution was added to the sample.

Series 1.—The reactor type A containing 3.00 g (before use) of the catalyst I was used, which was successively subjected to the various treatments. In runs 1 to 3 (Table 1 or Fig. 3), the catalyst was first weighed after each treatment, the cyanide yield was then determined at 650°C with the major portion of the weighed catalyst, and an X-ray pattern was taken of the minor portion. In runs 4 to 15 the yield was determined with the whole amount of the treated catalyst.

Series 2.—The catalyst II and the type B reactor containing asbestos was used. After each treatment the catalyst temperature was maintained for 6 hours at 650°C, while the cyanide yield was determined four times, and the quantity of unreacted ammonia, if at all, twice. As the catalyst granules were found somewhat disintegrated after every run of the series, the catalyst was sieved after every treatment as follows to use *ca.* 1.6 g of 8–14 mesh for the yield determination and *ca.* 0.3 g of 8–40 mesh for the surface area measurement throughout this series.

About 5 g of freshly prepared catalyst was first pretreated, and then divided into three portions; *ca.* 1.6 g of 8–14 mesh, *ca.* 0.3 g of 8–40 mesh, and the rest. The first portion was used for the yield determination and the second for the measurement of the surface area and the sulfur content, while the last was stored in a desiccator with no desiccant. After the yield was determined, the first portion was mixed with the stored one, and then subjected to the heat treatment. The heat-treated catalyst was again divided into three portions. This procedure was repeated occasionally with some modifications so as to subject the catalyst to various, successive treatments.

Series 3.—The catalyst II and the type B reactor was used without asbestos. After each treatment the catalyst temperature was maintained for 6 hours at 650°C, while the cyanide yield was determined four times.

About 8 g of freshly prepared catalyst was first pretreated, and then divided into two portions; *ca.* 1.6g of 8–14 mesh and the rest. With the former portion the yield, the surface area, and the sulfur content were successively determined. The latter was heat-treated and divided again into two portions, *i.e.*, *ca.* 1.6 g of 8–14 mesh and the rest. With the former portion, determinations were made of the yield, the surface area, and the sulfur content in succession. The latter portion was subjected to the water treatment (b), and then to the similar determinations as in the case of the former portion.

§ 3. Results

Series 1

The experimental conditions and results are summarized in Table 1 and

TABLE 1. Series 1: Successive treatments of catalyst.

Run	Condition of treatment			Effect of treatment				
	Kind	Temp. (°C)	Time	Catalyst				H$_2$S d)
				Weight (g)		Phase	Appearance	
				a)	b)			
	Fresh catalyst			3.00			white	
1	Pre.	650	9 hour	2.66	2.58	r-alumina	yellow	+
2	Heat	800	15 "			"	c)	+
		850	6 "					+
		900	11 "	2.56	2.41			+
3	H$_2$SO$_4$	b.p.	5 min	2.34	2.21	"	gray	
	Pre.	650	7 hour	2.08	1.98	"	"	+
4	Heat	900	28 "				"	+
		950	7 "	1.88				+
5	H$_2$O (a)	100	5 min	1.88			"	
6	Heat	800	7 hour				"	—
		900	5 "					—
		950	9 "	1.89				—
7	H$_2$O (a)	100	5 min	1.87			"	
8	Heat	950	5 hour	1.87			"	—
9	HO$_2$ (a)	100	5 min	1.87			"	
10	Heat	950	3 hour	1.86			"	—
11	H$_2$SO$_4$	b.p.	5 min	1.79			"	
	Pre.	650	2 hour					+
12	Heat	950	11 "	1.71			"	—
13	H$_2$O (a)	100	5 min	1.71			"	
14	Heat	950	13 hour	1.71			"	—
15	H$_2$O (a)	100	5 min	1.70		r-alumina	"	

b.p., boiling point of *ca.* 1N H$_2$SO$_4$.

a) After treatment or treatment plus cyanide yield determination.

b) After removing a minor portion as a sample of X-ray diffraction.

c) The appearance changed gradually from yellow to gray in the course of the treatment.

d) Whether hydrogen sulfide was detected (+) or not (−) in the gas leaving the reactor during pretreatment or heat treatment.

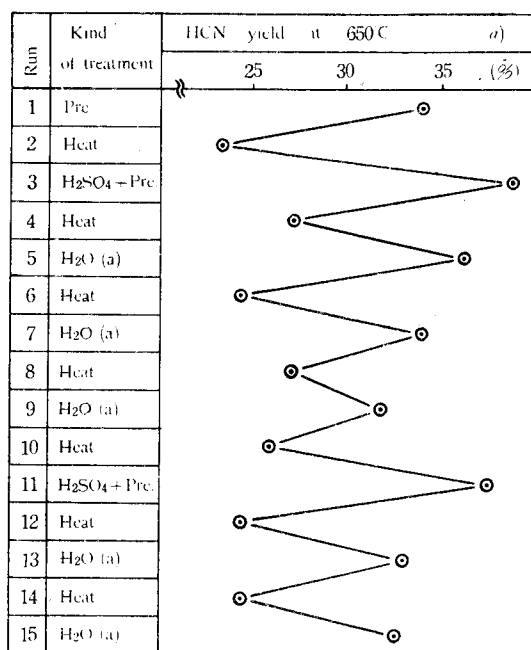| Run	Kind of treatment	HCN yield at 650°C a)

Fig. 3. Series 1: The Variation of cyanide yield with successive treatments of catalyst.

    a) The percentage conversion of ammonia into hydrogen cyanide.

Fig. 3. It is seen from the table that freshly prepared or sulfcric acid-treated catalyst loses weight by the next pretreatment or heat treatment. The sulfuric acid treatment also causes the catalyst to lose weight. The former loss would be due to the reduction of sulfate to sulfide and then to its liberation as hydrogen sulfide. The loss on the acid treatment would be due to the dissolution of alumina or thoria, since the supernatant acid solution, with which the catalyst has been treated, deposits white and flocculent precipitate when neutralized with caustic alkali. The crystal structure of the catalyst remains unchanged throughout the present series. As evident from Fig. 3, the cyanide yield reduced by the heat treatment can be restored by the acid or water treatment*). The acid treatment is somewhat superior in effect to the water treatment.

Series 2 and 3

Table 2 summarizes the experimental conditions and results except those

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 *) Asbestos present in the reactor, although initially inactive, was found to become catalytically active in the course of the series. The cyanide yields shown in Fig. 3 include the contribution from the asbestos placed above and below the catalyst bed.

TABLE 2. Series 2 and 3: Successive treatments of catalyst.

Series	Run	Condition of treatment			Effect of treatment					
		Kind	Temp. (°C)	Time	Catalyst		H_2S a)	X_{HCN} b)	X_{NH_3}	W c)
					S_1	Appearance				
Fresh catalyst						white				
2	1	Pre.	650	10 hour	148	yellow	+	{ 44.3 { 43.1		1.61 —
	2	Heat	900	12 ,,	106	bluish gray	+	{ 29.9 { 28.7	69.0 69.4	1.61 1.60
	3	{ H_2SO_4 { Pre.	b.p. 650	5 min 4 hour	116	,, ,,	+	{ 41.6 { 39.8	61.6 61.9	1.60 1.60
	4	Heat	950	9 ,,	96.5	,,	—	{ 28.6 { 27.9	71.3 72.0	1.60 1.61
	5	H_2O (a)	100	5 min	101	,,		{ 37.1 { 36.1	63.4 63.1	1.59 —
	6	Heat	950	9 hour		,,	—	{ 30.9 { 29.3		— 1.59
	7	H_2O (a)	100	5 min		,,		{ 35.7 { 34.6		— 1.60
	8	Heat	950	9 hour		,,	—	{ 28.6 { 27.8		— 1.61
	9	H_2O (a)	100	5 min	85.0	,,		{ 34.9 { 32.6		1.59 1.58
3	1	Pre.	650	10 hour	150	yellow	+	{ 42.8 { 42.0		1.61 1.61
	2	Heat	950	9 ,,	96.2	bluish gray	+	{ 27.6 { 27.1		1.62 1.61
	3	H_2O (b)	100	30 min	105	,,		{ 35.7 { 34.3		1.57 1.54

S_1, specific surface area; X_{HCN}, percentage conversion of ammonia into hydrogen cyanide at 650°C; X_{NH_3}, percentage of unreacted ammonia to fed ammonia at 650°C; W, weight of catalyst in gram used for the determinations of X_{HCN} and X_{NH_3}; b.p., boiling point of ca. $1N H_2SO_4$; feed rates of reactants, 100 cc/min of CO and 10 cc/min of NH_3.

a) Whether hydrogen sulfide was detected (+) or not (−) in the gas leaving the reactor during pretreatment or heat treatment.

b) Only the highest and the lowest values of four determinations are cited.

c) Catalyst weight was determined before (upper figures) and after (lower figures) the determinations of the cyanide yield.

concerning sulfur content. As shown in the table, the cyanide yield[*] decreases on heat treatment and increases on sulfuric acid or water treatment. This is in agreement with the change observed in Series 1. The change in surface area is parallel to that in the yield. The effect of the treatments will be furthur intvestigated below, introducing the rate constant of the synthetic reaction as the measure of the catalytic activity.

Rate Constant.—Let s be the cross-sectional area of the reactor, h the length of the catalyst bed in the direction of flow, w the weight of the catalyst per unit volume, and R the moles of hydrogen cyanide produced per unit time per unit weight of catalyst. Product $Rwsdh$ is now the moles of hydrogen cyanide produced per unit time by the portion of the catalyst between h and $h+dh$. The same quantity may be expressed also by $MdX/100$, where M is the moles of fed ammonia per unit time and X is the percentage conversion of ammonia into hydrogen cyanide, dX being the increment of X from h to $h+dh$. Thus

$$Rwsdh = MdX/100 . \qquad (2)$$

It has been proved experimentally by HORIUTI, *et al.*[7] that R is proportional to $X_e - X$, where X_e is the equilibrium percentage conversion of ammonia into hydrogen cyanide, *i.e.*,

$$R = k(X_e - X) , \qquad (3)$$

where k is a constant. We designate the k as rate constant. Substituting R from equation (3) into equation (2) and integrating over the whole catalyst bed, we have

$$k = 0.01 \frac{M}{W} \ln\left(\frac{X_e}{X_e - X}\right) , \qquad (4)$$

where W is the total weight of catalyst of the bed.

Fig. 4 shows the values of k and k/S_1, where S_1 is the specific surface area or the surface area per gram catalyst. They are calculated by equation (4), using the values 4.46×10^{-4} mole/min of M and 60.4[**] of X_e, from catalyst weight, cyanide yield, and specific surface area given in Table 2. Both k and k/S_1 as well as the yield decrease on heat treatment and increase on sulfuric acid or water treatment. The k is not, however, fully recovered by sulfuric

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*) Also in series 2, asbestos is present in the reactor. Its catalytic activity, however, is restrained to such a extent that its contribution to cyanide yield is at most 2 in percentage conversion of ammonia into hydrogen cyanide.

**) This value is calculated from an equilibrium constant of 7.18×10^{-3} at 650°C for the reaction (1) [Ref. 7].

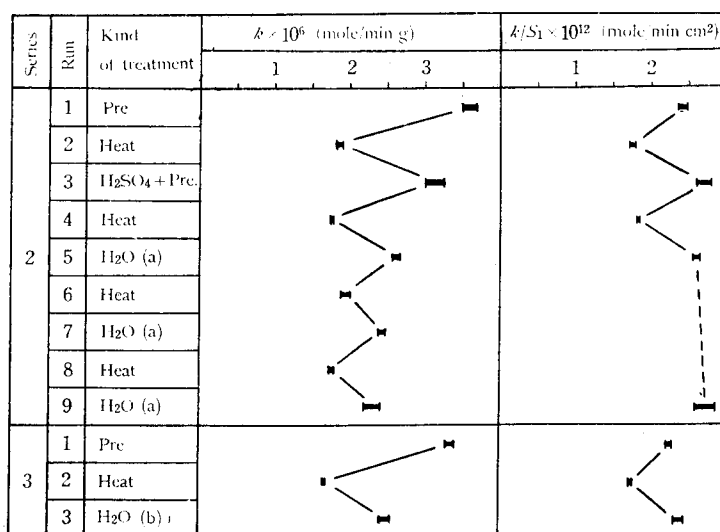| Series	Run	Kind of treatment	$k \times 10^6$ (mole/min g)			$k/S_1 \times 10^{12}$ (mole min cm²)	
			1	2	3	1	2
2	1	Pre					
	2	Heat					
	3	H_2SO_4 + Pre.					
	4	Heat					
	5	H_2O (a)					
	6	Heat					
	7	H_2O (a)					
	8	Heat					
	9	H_2O (a)					
3	1	Pre					
	2	Heat					
	3	H_2O (b)					

Fig. 4. Series 2 and 3: The variations of k and k/S_1 with successive treatments of catalyst.

k, rate constant (per gram catalyst); S_1, specific surface area of catalyst; reaction temperature, 650°C; feed rates of reactants, 100 cc/min of CO and 10 cc/min of NH_3.

acid or water treatment and depressed gradually with the repetition of treatment (1, 3, 5, 7, 9 of series 2, and 1, 3, of series 3) whereas no such trend is found with k/S_1.

Control of Sulfide Sulfur Analysis.—The method of sulfide sulfur analysis described in § 2 was controlled by analyzing known amounts of barium sulfide, sulfur, and sodium sulfate, with the results shown in Table 3. These results suggest that the method is not quantitatively applicable, but useful to find an approximate amount of sulfide sulfur.

TABLE 3. The control of sulfide sulfur analysis.

Kind of sample	Sample taken (mg)	S_C (mg)	S_F (mg)	$\dfrac{S_F}{S_C} \times 100$
Ba S	9.3	1.76	1.37	77.9
Ba S	24.1	4.56	2.88	63.2
S	12.5	12.5	0.05	0.4
Na_2SO_4	4.43	1.00	0.00	0.0

S_C, sulfur content (calc.); S_F, sulfur content (found).

Sulfur Content.—The results are shown in Table 4, where the value of "sulfate sulfur" in the last column is the difference between the preceding two values. It might be expected from Table 3 that the sulfide sulfur contents tabulated in Table 4 are lower bounds to the respective actual values, and hence

TABLE 4. Sulfur Content in weight Percent of Catalyst.

Series	Run	Treatment of catalyst	Total sulfur	Sulfide sulfur	Sulfate sulfur
		Fresh catalyst	8.17	0.000	8.17
2	1	Pre.	0.624	0.221	0.403
	2	Heat	0.107	0.048	0.059
	3	H_2SO_4+Pre.	0.138	0.027	0.111
	4	Heat	0.044	0.016	0.028
	5	H_2O (a)	0.042	0.019	0.023
	$\approx$				
	9	H_2O (a)	0.031	0.006	0.025
3	1	Pre.	0.630	0.162	0.468
	2	Heat	0.058	0.023	0.035
	3	H_2O (b)	0.045	0.024	0.021

the sulfate sulfur contents in the same table are upper bounds. Total sulfur as well as sulfate sulfur is lost a great deal by the initial pretreatment, and is furthur reduced by the subsequent treatments except by the sulfuric acid treatment followed by the pretreatment. No sulfide sulfur exists in the catalyst before use, but does after use as shown in the Table.

§ 4. Discussion

It is seen from the experimental results described in § 3 that the change in cyanide yield brought about by each treatment can be ascribed partly to the change in surface area of catalyst and partly to the change in k/S_1, *i.e.*, rate constant per unit surface area. Unfavorable side reactions, *e.g.*, the decomposition of ammonia and the disproportionation reaction, $2CO = CO_2 + C$, could hardly be responsible for the above effect on k/S_1, since they are shown practically absent[*].

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[*] Table 2 shows that the sum of cyanide yield and unreacted ammonia quantity is nearly 100 percent in each run, which evidences the practical absence of the decomposition of ammonia in the present work. The absence of the disproportionation reaction at 650°C is verified on the other hand by that of soot deposition, which is observed on asbestos and porcelain plate at or over 800°C.

It has been predicted theoretically by HORIUTI, *et al.*[8] that sulfuric acid possibly catalyzes the synthetic reaction of hydrogen cyanide. There seems, however, to be no distinct interrelation between k/S_1 and sulfate content, which varies over a very wide range through series 2 or 3. It remains thus to be elucidated why k/S_1 varies as observed by the treatments.

Summary

Alumina-thoria containing sulfate was employed as catalyst for the synthetic reaction of hydrogen cyanide from carbon monoxide and ammonia. Cyanide yield was determined at 650°C in a flow system under ordinary pressure. The yield decreases markedly on heat treatment of the catalyst carried out in a reactant stream at temperatures of 800 to 950°C. The deativated catalyst is easily regenerated to a considerable extent by sulfuric acid or water treatment. These changes in cyanide yield can be ascribed partly to the change in surface area of the catalyst and partly to the change in catalytic activity per unit surface area. The latter is not explained on the basis of either undesirable side reaction or sulfate content, and remains to be elucidated.

Acknowledgment

References

1) a) J. HORIUTI, T. SATO and K. ISHIZUKA, U. S. Patent 2,889,201 (1959).
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Note: References 2), 7) and 8) are written in Japanese.